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CONCLUSIONS

1. The characteristics of extraction of phosphoric acid from Kovdor apatite concentrate depend mainly on the content of acid-soluble impurities. The ratio of MgO to P_2O_5 , up to 2.5% in the apatite has little influence on the extraction characteristics: during production of acid containing 30-31% P_2O_5 , $K_{decomp} = 97-98\%$, $Q_f = 1800-2000 \text{ kg}/(m^2 \cdot h)$.

2. Increase of the MgO/P_2O_5 ratio above 5% has an adverse effect on decomposition of apatite and crystallization of gypsum: $K_{decomp} = 88-91\%$, $Q_f = 500-600 \text{ kg}/(m^2 \cdot h)$.

3. At the same MgO/P_2O_5 ratio the characteristics of phosphoric acid extraction are better with Kovdor than with Khibiny apatite concentrate.

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INVESTIGATION OF ORGANIC IMPURITIES IN YELLOW PHOSPHORUS

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Technical yellow phosphorus (State All-Union Standard GOST 8986-75) contains up to 1.0% of organic impurities [1], on the composition of which there is no information at all. These impurities have a significantly adverse effect on the quality of products obtained from yellow phosphorus, favoring formation of resinous compounds and conferring a dark color on the products. In practical production of salt-free phosphorus derivatives there are as yet no agreed methods for assessment of the quality of phosphorus and determination of the influence of impurities in phosphorus on the quality of products synthesized from it.

Successful development of methods for determination of the qualitative composition of phosphorus and of more effective methods for its purification is possible only when the structure, composition, and properties of the organic compounds present as impurities in phosphorus have been established.

There have been no previous studies of the isolation and identification of these impurities. There has only been a general suggestion that the organic impurities in yellow phosphorus are hydrocarbons of high molecular weight; in particular, aromatic compounds [2]. It is noted [1] that the sources of these impurities in yellow phosphorus may be organic compounds present in phosphate rocks.

Some authors [3, 4] state that the organic compounds are probably volatile components from coke and electrode materials. It is also noted [4] that the volatile products formed during coking of the electrode mass consist of H_2 , CH_4 , CO , C_mH_n , N_2 and a certain amount of

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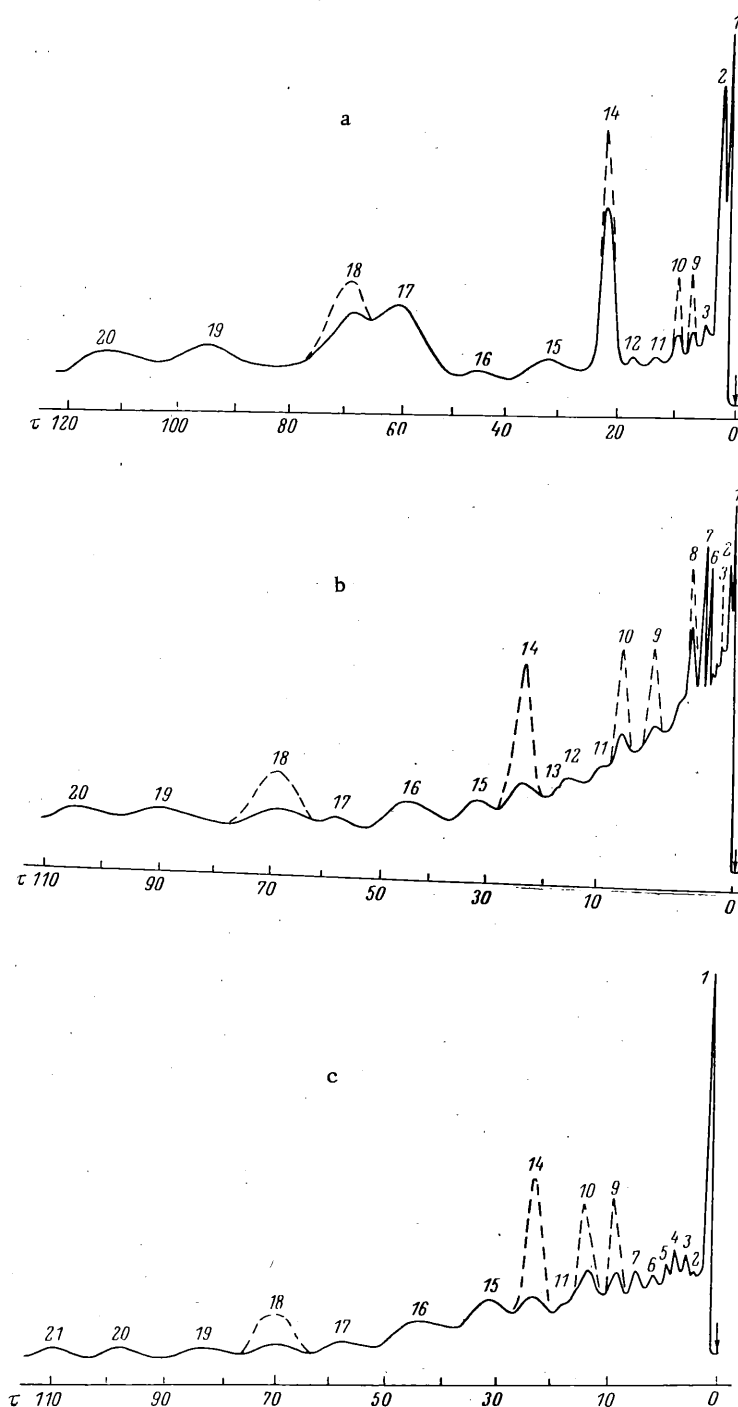


Fig. 1. Chromatograms of extracts from yellow phosphorus (a), coke (b), and phosphate ore (c). τ) Time (min). Identified components: a) 1) Solvent; 2) phosphorus; 9) diphenylene oxide; 10) diphenylene sulfide; 14) phenanthrene and anthracene; 18) carbazole and pyrene; b) 1, 9, 10, 14, 18) the same as for a; 3) durene; 8) biphenyl; c) 1, 9, 10, 14, 18) the same as for a.

complex hydrocarbon derivatives, including phenols, which seep through the electrode pores in the coking zone into the lower regions of the electrode, enter the reaction space of the furnace, and mix with the furnace gases. Thus, there is no exact information on the sources of the organic impurities in phosphorus.

For determination of the character of the impurities, we extracted organic compounds from phosphorus by treating it at 60°C with benzene-pyridine mixture (1:1), which has high solvent power for organic compounds of various classes. Technical yellow phosphorus conforming to GOST 8986-75, containing 0.1% of organic impurities, was taken for the experiments. The solvents of cp grade were distilled and dried over calcium chloride before the experiments. The extraction was conducted by treatment of portions of phosphorus (50 g) with 100 ml of the extractant with rapid stirring for 40-60 min. At the end of this time the mixture was settled, phosphorus was drained off through a stopcock at the bottom of the extractor, and a fresh portion of phosphorus was added to the original mixture. The total amount of phosphorus treated was 2 kg/100 ml of extractant. The dingy yellow color of the original phosphorus changed to translucent white after the treatment.

Steam distillation was used for organic compounds from coke and phosphate ore. Coke samples (corresponding to GOST 18686-73) containing 80% of particles 3-25 mm in size and 1-1.5% of volatile matter, and samples of phosphate ore from the Dzhankatas deposits were taken for the investigation.

The coke and phosphate ore samples (1-1.2 kg) were put into a steel tube fitted with an inlet and an outlet tube for superheated steam and a thermocouple socket. The filled tube was inserted into a shaft furnace and heated to 180-200°C, after which superheated steam was passed into the tube and the temperature was raised. In the case of coke samples copious evolution of yellow-green smoke and condensation of brown tarry compounds of organic origin occurred even at the stated temperature. Some of these compounds formed an oily layer on the surface of the condensate while the rest, insoluble in water, settled in the form of tar. The process was stopped when a temperature of 1000-1100°C was reached.

In the case of phosphate ore intensive evolution was not observed visually, while the condensate in the receiver had a dark color owing to the presence of finely divided solid particles, easily separated by filtration. Organic compounds were extracted into benzene from the condensates. The surfaces of the coke and phosphate-ore samples after the steam treatment were also treated with benzene. The extracts from the condensates were mixed with the extracts from surface treatment of the materials and concentrated after a considerable proportion of the solvent had been blown out by nitrogen at 40-50°C.

The isolated compounds were identified with the aid of gas chromatography (with the Tsvet-102 instrument). A glass column 3 m long and 3 mm in diameter, packed with Chromaton N-AW impregnated with a 5% solution of silicone XE-60, was used for separation of the mixtures. The temperature in the evaporator was maintained at 400°C, and in the column thermostat at 200°C. Nitrogen was used as the carrier gas; the detector was of the flame ionization type. The original samples were introduced in liquid form (0.1-0.4 µl). The chromatograms of extracts from phosphorus, coke, and phosphate ore are shown in Fig. 1.

According to the number of peaks, the phosphate ore and coke contain a larger number of organic compounds than phosphorus. The peak emergence times indicate that phosphorus contains predominantly high-boiling compounds while coke and phosphate ore also contain certain amounts of low-boiling components.

Preliminary investigations of the extracts by UV spectroscopy showed that strong absorption peaks of the isolated compounds lie in the region of 210-390 nm, which is characteristic of absorption by higher aromatic compounds such as anthracene, phenanthrene, pyrene, chrysene, biphenyl, carbazole, etc. The closest similarity of the spectra of the extract from phosphorus and of a solution of coal tar, the composition of which has been adequately studied [5], should be noted.

Compounds such as durene, biphenyl, acenaphthene, diphenylene oxide, diphenylene sulfide, anthracene, phenanthrene, carbazole, chrysene, and pyrene were used for identification. These compounds were dissolved in benzene and their emergence times under constant chromatographic conditions were determined.

Yellow phosphorus, which dissolves in the benzene-pyridine mixture during extraction, ionizes the flame during combustion in the detector and also gives a peak on the chromatogram

TABLE 1. Contents of Organic Impurities in Phosphorus and Raw Materials

| Materials | Contents of organic impurities (mg) in 1 kg of materials (calculated per kg of phosphorus) | | | |
|--------------------------------------------|-----------------------------------------------------------------------------------------------|------------------------|--------------------------------|-------------------------|
| | diphenylene oxide | diphenylene sulfide | anthracene and phenanthrene | carbazole and pyrene |
| Phosphate ore | 1.2 (13.2) | 1.4 (15.4) | 2.1 (23.1) | 6.2 (68.2) |
| Phosphate - clay shale | 0.8 | 0.42 | 6.3 | 20.2 |
| Coke | 54.0 (92.0) | 60.0 (102.0) | 121.0 (205.0) | 83.0 (141.0) |
| Coal-tar pitch in electrode mass [6] | 11 000 (99) | 4000 (36) | 60 000 (540) | No quantitative data |
| Phosphorus | 3.1 | 4.7 | 108.0 | 521.0 |

(Fig. 1a). Therefore the emergence time of phosphorus was determined in the course of the investigation. It was found that anthracene and phenanthrene, being isomers having similar boiling points (354.5 and 340°C respectively) are not separated on the given stationary phase and have the same emergence time on the chromatogram. Pyrene and carbazole also have the same emergence time.

To judge from the agreement of the emergence times and the character of the peaks on the chromatograms of the individual components and of extracts from phosphorus, coke, and phosphate ore, durene and biphenyl were present only in coke; diphenylene oxide, diphenylene sulfide, phenanthrene, anthracene, carbazole, and pyrene were present both in phosphorus and in all the components used for its production (Fig. 1, parts a-c, peaks 9, 10, 14, 18). The presence of these compounds is also confirmed by the increase of peak intensities when individual compounds were introduced into the extract (indicated by dashed lines).

The contents of the identified compounds in coke, phosphorus, and phosphate ore were estimated by comparing peak areas on the chromatograms of the extracts with areas of the peaks of the pure components present in known concentrations. Anthracene and phenanthrene solutions of equal concentration gave peaks of equal area on the chromatograms; therefore their total contents were estimated.

The results of quantitative determinations, correct within $\pm 20\%$, are given in Table 1.

The amounts of impurities per kg of phosphorus introduced with the charge were calculated from the amounts of materials: phosphate ore ~ 11 kg, coke ~ 1.7 kg [3], and electrode mass containing 15% pitch ~ 0.07 kg [7]. According to our data, the total content of such compounds as diphenylene oxide, diphenylene sulfide, anthracene, phenanthrene, carbazole, and pyrene is ~ 0.65 g per kg of phosphorus, or 70% of all the organic compounds in the phosphorus studied. The degree of transfer is 1.0-1.5% of relatively low-boiling organic compounds (diphenylene oxide, diphenylene sulfide), and 15% of anthracene and phenanthrene. However, the amount of carbazole and pyrene in 1 kg of phosphorus is 2.5 times the content in the same amounts of coke and phosphate ore expended for its production. This partially supports the possibility of emergence of coking gases from the electrode mass into the furnace space, although increase of the amount of carbazole and other carbon-saturated compounds (pyrene, chrysene) as the result of carbaonization at a high temperature in a reducing medium is not ruled out.

Investigation of the extract by capillary chromatography in a steel column 100 m long and 0.3 mm in diameter, with OV-17 as the stationary phase, additionally demonstrated the presence of fluorene, acenaphthene, fluoranthene, pyrene, chrysene, 1,2-benzoanthracene, 7,12-dimethylbenzoanthracene, and 1,2-benzopyrene. Unidentified impurities comprise 10-15% of the total content of organic compounds. At the same time separation of phenanthrene and anthracene, and of carbazole and pyrene, was achieved, and the presence of small amounts of biphenyl and naphthalene, not detected by us in the 3-meter column, in phosphorus was demonstrated.

Increase of the contents of anthracene, phenanthrene, carbazole, and pyrene in shales may presumably lead to a certain increase of the contents of these impurities in phosphorus if shales are introduced into the charge. The absence of low-boiling compounds in phosphorus is explained by their relatively low condensation temperatures. Evidently, the volatile components whose boiling points are close to that of phosphorus and which are also readily miscible are condensed predominantly with phosphorus and become distributed in it. The more volatile components, such as phenols, are carried out with flue gases and wastewaters [4].

Thus, the organic impurities in yellow phosphorus are higher aromatic and heterocyclic compounds with two or more rings in the molecule. According to the chromatograms, phosphorus contains more than 30 different organic compounds, 15 of which were identified by us. The following comprise about 70% of their mass: diphenylene oxide (bp 288°), diphenyl sulfide (bp 331.4°), phenanthrene (bp 340°), anthracene (bp 354.5°), carbazole (bp 354.7°), and pyrene (bp 394°), together with certain amounts of naphthalene (bp 218°), biphenyl (bp 258°), acenaphthene (bp 277°), fluorene (bp 295°), fluoranthene (bp 384°), chrysene (bp 440.7°), 1,2-benzoanthracene (bp 438°), 7,12-dimethylbenzoanthracene (bp 440°), and 1,2-benzopyrene (bp 450°). In addition to these compounds, phosphorus contains a number of unidentified hydrocarbons.

CONCLUSIONS

1. The presence of naphthalene, biphenyl, acenaphthene, diphenylene oxide, diphenylene sulfide, fluorene, anthracene, phenanthrene, carbazole, fluoranthene, pyrene, 1,2-benzoanthracene, chrysene, 7,12-dimethylbenzoanthracene, and 1,2-benzopyrene in phosphorus was demonstrated by identification of chromatograms. Their quantitative contents were estimated.
2. The main organic compounds present as impurities are phenanthrene, anthracene, carbazole, and pyrene.

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